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THEORETICAL STUDIES OF IONIC AND ATOMIC
IMPACT PHENOMENA

By

RONALD E. OLSON and FELIX T. SMITH

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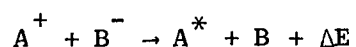
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ABSTRACT

An "absorbing-sphere" model based on the Landau-Zener method was developed for calculating the energy dependence of the total cross sections for the reaction



in which A or B may be atomic or molecular species. It was found that the cross sections were highly dependent on the electron detachment energy of B^{-} . In a second research task, the ionization (Penning and associative) total cross sections for $Ne^{*}(2p^5 3s \ ^3P) + Ar$ were calculated over a large energy range and compared with the experiments of Micha, Tang, and Muschlitz.

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INTRODUCTION

The main objectives of the research under this contract are to perform fundamental studies in the field of low-energy electronic, ionic, atomic, and molecular impact phenomena. The theoretical studies are related to this laboratory's experimental investigations of low-energy collisions and processes that are important to the understanding of the upper atmosphere. This research is a continuation of the work under Contract No. NASr-49(07), SRI Project No.-4070.

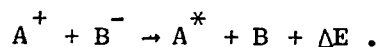
SUMMARY OF RESULTS

During the period of this contract, two separate research tasks were completed. The first, which was also partially supported by a DNA project, consisted of theoretically predicting the cross section energy dependence for ion-ion recombination of molecular species. The results were compared with existing experimental measurements. A second research task consists of trying to understand the unexpected energy dependence of the ionization cross sections measured by Micha, Tang, and Muschlitz on the $\text{Ne}^* + \text{Ar}$ system.

Both of these works have just recently been submitted for publication. A summary of the results is given below, and a more detailed description is given in the appendices.

A. Ion-Ion Recombination Total Cross Sections

A procedure has been set up for calculating the total cross sections for the ion-ion recombination reaction



The method was developed especially for the cases where A or B are complicated molecular species and where more exact calculations are not possible. The procedure is based on the Landau-Zener method for calculating the inelastic cross sections. A semiempirical method has been developed¹ with which to estimate the necessary coupling matrix elements as a function of the crossing distance R_x so that calculations can be made (the coupling matrix element research was supported by NASA by the contract that preceded this one). We have previously used the Landau-Zener method to compute the ion-ion recombination cross sections as a function of energy for the systems $H^+ + H^-$, $He^+ + H^-$, $O^+ + O^-$, and $N^+ + O^-$, and we have found it to work surprisingly well² (this research was also supported by the preceding NASA contract). The multistate Landau-Zener calculations included many states and, as an example, in the $N^+ + O^-$ reaction, there were approximately 25 channels (excited electronic levels) available for reaction. If we proceed to molecular systems, we find that the number of available channels increases dramatically because of the large number of electronic, vibrational, and rotational states available.

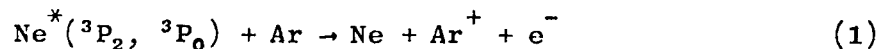
This leads us to the assumption that for the more complicated systems we may approximate the physical situation by using a high density of crossing states. Then by using the Landau-Zener method and the semiempirical coupling matrix elements, we may obtain a critical crossing distance R_c within which there will be reaction. From R_c , the total cross sections can be calculated by assuming an absorbing-sphere model, i.e., unit probability for reaction within R_c .

For the systems studied experimentally, we find good agreement between theory and experiment for cases where there is an atomic negative ion, but for the molecular negative ion systems we find the theory tends to underestimate the magnitude of the reaction rate obtained from extrapolation of the merged-beam results. In the reaction rate calculations, the cross sections are mainly determined by the electron detachment energy of the negative ion with lower electron detachment energies producing larger cross sections (the degree of excitation of the positive ion plays only a small part). We believe that since experimentally the negative ions are formed in a duo-plasmatron under very hot conditions, it is not unlikely that the molecular ions are formed in excited electronic or vibrational states. This would lead to an observed cross section that is larger than the calculated one, which is based on the assumption that the ions are in their ground states. This would also explain the reason why the more complicated atomic systems are in agreement with theory since the excited levels are not available to atomic negative ions. Further work, both experimental and theoretical, will be needed to verify these predictions.

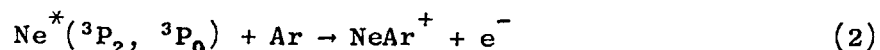
A complete description of the above work is presented in Appendix A and has been accepted for publication in The Journal of Chemical Physics³.

B. Ne* + Ar Ionization Total Cross Sections

The recent experimental data of Micha, Tang, and Muschlitz⁴ on the low energy (0.01 to 0.1 eV) dependence of the ionization total cross sections for the sum of the Penning ionization process



and of the associative ionization process



display an unexpected energy dependence that has not been explained by theoretical calculations. These authors find cross sections that first decrease as the energy increases, then pass through a minimum, and later increase at the highest energies measured. Calculations by these authors using a Lennard-Jones, L-J, (12,6) interaction potential and a short range coupling width $\Gamma(R)$ were able to reproduce the low energy, monotonically decreasing behavior of the cross sections but did not follow the change in slope. Further experimental work by Tang, Marcus, and Muschlitz⁵ on $\text{Ne}^* + \text{Kr}$ and $\text{Ne}^* + \text{Xe}$ show the same type of behavior. On another noble gas system-- $\text{He}^*(2^3\text{S and } 2^1\text{S}) + \text{Ar}$ --the thermal energy cross section is comparable to or smaller than the high energy results at 100 to 1000 eV. It therefore appears that the shape of the energy dependence of the $\text{Ne}^* + \text{Ar}$ cross sections could be common to many of the noble gas ionization reactions.

We have found that the $\text{Ne}^* + \text{Ar}$ data can be reproduced with the same L-J (12,6) Potential that is used in Ref. 4 if the coupling width has a more realistic exponential form. Furthermore, calculations at high energies, $E \approx 100$ eV, indicate that the ionization cross section is of the order of 10 \AA^2 . This is similar in magnitude to the high energy experimental results for $\text{He}^* + \text{Ar}$ that have been measured here⁶.

Since the experimental measurements are most conveniently made at thermal energies, $E \lesssim 0.1$ eV, and at high energies, $E \gtrsim 100$ eV, the theoretical technique provides a means of interpolating the cross sections to the energy region 0.1 to 1.0 eV, the region of interest for upper atmosphere processes.

A more complete description of this work is given in Appendix B. The manuscript has been submitted to Chemical Physics Letters for publication.

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LIST OF APPENDICES

- Appendix A "Absorbing-Sphere Model for Calculating Ion-Ion Recombination
Total Cross Sections", R. E. Olson.
- Appendix B "Energy Dependence for $\text{Ne}^*(2p^5 3s \ ^3p) + \text{Ar}$ Ionization Total
Cross Sections", R. E. Olson.

Appendix A

ABSORBING-SPHERE MODEL FOR CALCULATING ION-ION RECOMBINATION TOTAL CROSS SECTIONS

ABSORBING-SPHERE MODEL FOR CALCULATING
ION-ION RECOMBINATION TOTAL CROSS SECTIONS^{*}

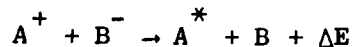
by

Ronald E. Olson

Stanford Research Institute
Menlo Park, California 94025

ABSTRACT

An "absorbing-sphere" model based on the Landau-Zener method is set up for calculating the upper limit thermal energy (300°K) reaction rate and the energy dependence of the total cross sections for the ion-ion recombination reaction



in which A or B may be atomic or molecular species. The crucial parameter needed for the calculation is the electron detachment energy for the outer electron on B⁻. For a given system and energy, we find that, as the electron detachment energy is decreased because of the existence of metastable electronic states or excited vibrational states, the cross sections increase. The calculated cross sections and rates are compared with afterglow results and with those obtained from "merged-beam" experimental data. We find good agreement with the existing results for atomic negative ions. There are differences for molecular negative ions, and the possible cause of these differences is discussed.

INTRODUCTION

The theoretical development for the calculation of the total cross sections for the ion-ion recombination reaction



may take one of two principal paths. The first, and most exact, is to calculate the ab initio potential energy surfaces for all the electronic states of reaction (1) and then to perform coupled-channel calculations to obtain the appropriate transition probabilities from which total cross sections may be computed. This method is time consuming, and the calculations have been performed only for the simplest reaction, that of $H^+ + H^-$. The second approach is to use semiempirical methods to calculate the parameters needed to obtain reasonable estimates of the cross sections. This is the procedure that is described here. We will be concerned with estimating the thermal energy (300° K) reaction rate and the energy dependence of the cross sections for reaction (1) when A or B or both may be atomic or molecular species. In particular, we will be concerned with species of upper atmosphere importance, since reaction (1) is an important mechanism in the final removal of charge in the D region of the atmosphere.^{2,3}

The procedure to be described is based on the Landau-Zener method for calculating the inelastic cross sections.⁴⁻⁷ A semiempirical method has been developed⁸ with which to estimate the necessary coupling matrix elements H_{12} as a function of the crossing distance R_x so that calculations can be made. We have previously used the Landau-Zener method to compute the ion-ion recombination cross sections as a function of energy for the systems $H^+ + H^-$, $He^+ + H^-$, $O^+ + O^-$, and $N^+ + O^-$, and we have found it to work surprisingly well.^{9,10} The multistate Landau-Zener calculations

included many states and, as an example, in the $N^+ + O^-$ reaction, there were approximately 25 channels (excited electronic levels) available for reaction. If we proceed to molecular systems, we find that the number of available channels increases dramatically because of the large number of electronic, vibrational, and rotational states available.

This leads us to the assumption that for the more complicated systems we may approximate the physical situation by using a high density of crossing states. Then by using the Landau-Zener method and the semiempirical coupling matrix elements, we may obtain a critical crossing distance R_c within which there will be a reaction. From R_c , the total cross sections can be calculated by assuming an absorbing-sphere model, i.e., unit probability for reaction within R_c .

We have compared our results with those obtained from an extrapolation of merged-beam data to thermal energies⁹⁻¹⁴ and also with some afterglow measurements.^{15,16} In the systems studied experimentally, we find good agreement between theory and experiment for cases where there is an atomic negative ion, but for the molecular negative ion systems we find the theory tends to underestimate the magnitude of the reaction rate obtained from extrapolation of the merged-beam results. Possible reasons for this discrepancy are given in a later section.

The energy dependence of the total cross sections may also be estimated by using the absorbing-sphere model. As in the reaction rate calculations, the cross sections are mainly determined by the electron detachment energy of the negative ion with lower electron detachment energies producing larger cross sections. Comparisons are made with experimental merged-beam data for several O^- systems, and the energy dependence of the cross sections is found to be well reproduced. The theoretical cross section energy dependence for several other negative ion systems is also given.

THEORY

To determine the critical distance R_c within which there is reaction, it is best to review the application of the two-channel Landau-Zener method to reaction (1). It will then be possible to ascertain the functional dependence of the crossing parameters on the cross sections and to extend these results to the multicrossing case.

In the two-state Landau-Zener approximation, the total cross section is given by (all quantities will be in atomic units)

$$Q_{12} = 4\pi R_x^2 (1 + \Delta E/E) F_3(\lambda) \quad , \quad (2)$$

where $F_3(\lambda)$ is the tabulated exponential integral^{5,6}

$$F_3(\lambda) = \int_1^\infty e^{-\lambda x} (1 - e^{-\lambda x}) x^3 dx \quad , \quad (3)$$

and λ is related to the velocity v and crossing parameters by

$$\lambda = \frac{2\pi H_{12}^2(R_x)}{\left| V_1' - V_f' \right| v (1 + \Delta E/E)^{1/2}} \quad . \quad (4)$$

In Eq. (4), H_{12} is the coupling matrix element evaluated at the crossing distance R_x , and V' is the derivative of the potential with respect to R at R_x . For ion-ion recombination in which we have a Coulomb potential crossing a dipole-induced dipole R^{-6} potential at large distances, $R \gtrsim 15$ a.u., it is a good approximation to let¹⁷

$$\left| V_i' - V_f' \right| = R_x^{-2} \quad (5)$$

and

$$\Delta E = -V_i(R_x) = R_x^{-1} \quad (6)$$

Substituting Eq. (5) into Eq. (4), we have

$$\lambda = \frac{\sqrt{2} \pi R_x^2 \mu^{1/2} H_{12}^2(R_x)}{(E + \Delta E)^{1/2}} \quad (7)$$

We may make a further approximation for the special case of thermal energy. Since the important range of crossings lies between 15 and 50 a_0 , we find from Eq. (6) that ΔE lies between 0.5 and 2.0 eV. Therefore, at thermal energies $\Delta E \gg E$, so that by substituting Eq. (6) into Eq. (7) we arrive at the thermal energy result for λ :

$$\lambda = \sqrt{2} \pi R_x^{5/2} \mu^{1/2} H_{12}^2(R_x) \quad (8)$$

In the two-channel case, $F_3(\lambda)$ has a maximum value of 0.113 when λ is equal to 0.424.

If we now extend these results to the multichannel case where there are a large number of states available, we may expect complete reaction for values of R less than R_c where R_c is the value of the crossing distance that satisfies $\lambda = 0.424$ in Eq. (8). The total cross section from Eq. (2) will then be

$$Q = \pi R_c^2 [1 + (R_c E)^{-1}] \quad (9)$$

To determine λ , we must know its dependence on R . The coupling matrix element H_{12} is the only unknown, but from previous work on one-electron transfer, we have been able to parametrize it in terms of the effective ionization potential of the reactants and products.⁸

We may write the coupling matrix element in the reduced form

$$H_{12}^* = 1.044 R^* \exp(-0.857 R^*) \quad , \quad (10)$$

where

$$H_{12}^* = \frac{H_{12}}{I_1^{1/2} I_f^{1/2}} \quad ,$$

and

$$R^* = \frac{(\alpha + \gamma)R}{2} \quad . \quad (11)$$

The quantity α equals $(2I_1)^{\frac{1}{2}}$, where I_1 is the detachment energy of the electron being transferred, in a.u. For a ground state negative ion, I_1 is equal to the electron affinity. The quantity γ equals $(2I_f)^{\frac{1}{2}}$, where I_f is the effective ionization potential of the transferred electron in its product state. Equation (10) is valid only at large distances, $R \gtrsim 10$ a.u., where the electron is transferred through the potential barrier determined by the exponential tails of the wave functions for the reactant and product states and for values of I_1 and I_f greater than ~ 0.4 eV.

By knowing the electron detachment energy of the negative ion and by assuming that there is a high density of states available for reaction, we may then determine γ as a function of R by using the relationship

$$I_f = I_1 + R^{-1} \quad (12)$$

Using Eqs. (10) and (11), it is now an easy matter to obtain λ , Eq. (7), as a function of R . From numerical calculations using

large numbers of final states, we find that the value of λ to use for determining R_c for the multichannel case is approximately 0.15. The value $\lambda = 0.424$, which is correct for the two-channel case, tends to underestimate the value of the cross section by about 10%. The use of $\lambda = 0.15$ to determine R_c has been verified by Landau-Zener calculations employing large numbers of product channels. For a realistic system where there obviously is not a continuum of product states available, the model continues to work since each state can now accommodate a higher percentage of the total reaction probability due to less competition with neighboring channels. The cross sections are reduced by only 20% when there are as few as 5 product states.

The formulas presented above are contingent on a high density of states being available for reaction. In reality, there may be significantly fewer, so that the cross sections calculated from the above formulas should be an upper limit on the true situation.

Because of the Coulomb attraction, the product $E \cdot Q$ approaches a constant at thermal energies, Eq. (9), so that the reaction rate α , which is an average over a Maxwellian distribution of ion velocities, becomes

$$\alpha = 4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} \int_0^{\infty} Q \exp \left(-\frac{\mu v^2}{2kT} \right) v^3 dv \approx 2(v^2 Q) \left(\frac{\mu}{2\pi kT} \right)^{1/2}. \quad (13)$$

For molecular systems, the coupling matrix elements, Eqs. (10) and (11), should be modified by the Franck-Condon factors q that represent the overlap of the vibrational energy levels to read⁴

$$H_{12}^* = 1.044 q^{1/2} R^* \exp(-0.857 R^*) \quad . \quad (14)$$

The Franck-Condon factors are quantities less than unity, so again we find that we have an upper limit on the cross section. For the cases to be studied, even if all q_n were set equal to 0.1, the cross sections would be decreased by only about 20%.

Within the absorbing-sphere model described above, we find that the cross section is dependent only on the value of the electron detachment energy of the negative ion and the reduced mass of the system. A similar result is obtained in the work of Radtsig and Smirnov¹⁸ who use a different approach to this problem.

In a given system, as the electron detachment energy is decreased because of vibrational or electronic excitation, the reaction rate increases. Physically, this corresponds to the outer electron on the negative ion being more loosely bound, making it possible for transfer to occur at larger intermolecular separations. If the negative ion is present in an excited electronic or vibrational state, we would predict that the reaction rate will generally be greater than when the negative ion is in its ground state. This problem usually arises with molecular negative ions, but there may be some difficulty with an atomic negative ion system if the negative ion can be present in a metastable electronic state, such as C^- .

To remove some of the objections to using the Landau-Zener model, namely the tunneling problem, we have compared the Landau-Zener transition probabilities with the close-coupled values tabulated in reduced form by Delos.¹⁹ We find that the cross sections obtained by the Landau-Zener method are below the exact results and should be increased by approximately 10%. This factor has been included in our results.

THERMAL ENERGY REACTION RATES

Atomic Negative Ions

The above formulas were first applied to systems in which the negative ion was an atomic state. For these cases, the electron detachment energy is equal to the electron affinity. Since this quantity is well known, the calculations are straightforward. The results for several systems are given in Table I. In Table I, the \pm limits on the theoretical reaction rates correspond to what we consider to be reasonable limits on the accuracy of the H_{12} generator. By comparing the matrix elements with existing experimental and theoretical data of H_{12} vs R_x for one-electron transfer cases, we find that 85% of the data lie within a factor of 3 of the form given in Eqs. (10) and (11). The limits shown on Table I correspond to the factor of 3 limits on H_{12} .

For the atom-atom systems, we find good agreement with the extrapolated mercury beam results. One exception, however, is the $H^- + H^+$ system. Here, the theory overestimates the reaction rate. This result is not surprising, however, since for this system at thermal energies, only one channel (the $n=3$ excited state of H) is open for reaction. The assumption that there are a large number of states available for reaction is invalid in this case, leading us to obtain an upper limit reaction rate considerably above the experimental result. For the $O^- + O^+$, $O^- + N^+$, and $O^- + Na^+$ reactions, the agreement with experiment is good. In these cases, we would expect reasonable agreement because there are a large number of channels available for reaction.

TABLE I

ION-ION THERMAL ENERGY RECOMBINATION REACTION RATES:

ATOMIC NEGATIVE ION

System	Electron Detachment Energy (eV)	R_c (a.u.)	Calculated $\alpha \times 10^8 (\text{cm}^3/\text{sec})$	Experimental $\alpha \times 10^8 (\text{cm}^3/\text{sec})$
$\text{H}^- + \text{H}^+$	0.7542	24	90 ± 34	39 ± 21^a
$\text{D}^- + \text{He}^+$	0.7542	26	59 ± 20	--
$\text{D}^- + \text{H}_2^+$	0.7542	25	67 ± 23	47 ± 15^b
$\text{O}^- + \text{Na}^+$	1.478	23	20 ± 6	21 ± 10^c
$\text{O}^- + \text{O}^+$	1.478	23	22 ± 6	27 ± 13^a
$\text{O}^- + \text{N}^+$	1.478	23	22 ± 6	26 ± 8^a
$\text{O}^- + \text{O}_2^+$	1.478	24	19 ± 5	10 ± 4^c
$\text{O}^- + \text{N}_2^+$	1.478	23	20 ± 6	--
$\text{O}^- + \text{NO}^+$	1.478	23	19 ± 6	49 ± 20^c

a. Reference 13.

b. Reference 20.

c. Reference 14.

For the atom-molecule systems, experimental data exist on the $D^- + H_2^+$, $O^- + O_2^+$, and $O^- + NO^+$ reactions. Of these, there is satisfactory agreement between theory and experiment for the first two reactions with theory predicting larger reaction rates than observed. The $O^- + NO^+$ reaction is puzzling, however, since the experimental result is more than a factor of 2 larger than theory. Within the framework of this theory, there is no satisfactory explanation of this result.

For all the above cases, the reaction radius R_c is displayed in Table I. In these reactions, the most favorable transfer of the electron occurs at about 25 a.u. or at $\Delta E \approx 1$ eV. The electron affinities were taken from the review by Berry.²¹

Molecular Negative Ion

In systems in which the negative ion is molecular, the main difficulty in applying the absorbing sphere model is the determination of the correct electron detachment energy. In these cases, the negative ion may reside in an excited rotational or vibrational level or possibly in a metastable electronic state. Experimentally, how the negative ion is formed largely determines this final state. Compounding this problem is the fact that accepted values for electron affinities for most molecular species of atmospheric interest are generally not well known. Consequently, we have performed the calculations with the latest values for the electron affinities, which should be reasonably close to the real electron affinities.

Of considerable interest to the chemistry of the upper atmosphere are the neutralization reactions of O_2^- . For the calculations on the O_2^- systems, we have used a recently obtained value for the electron

affinity.²² In Table II, we find both merged-beam and afterglow results from the $O_2^- + O_2^+$ reaction. The theoretical value of $24 \times 10^{-8} \text{ cm}^3/\text{sec}$ for an electron detachment energy of 0.43 eV is almost a factor of 2 below the merged-beam value. However, the theoretical reaction rate is in agreement with an afterglow experimental value of $10 \times 10^{-8} \text{ cm}^3/\text{sec}$. In this latter case, the negative ions are formed at thermal energies so that the electron detachment energy should be close to the electron affinity. In the merged-beam experiments the ions are formed in dualplasmatron discharge sources so we might expect excited negative ions. For example, when the negative ions were formed by electron bombardment in an experiment by Burch, Smith, and Branscomb,²³ these authors found an electron detachment energy of $0.15 \pm 0.5 \text{ eV}$, which probably means that the ions were formed in an excited vibrational level. The reaction rate can then be expected to be larger than the calculated value, and calculations show the reaction rate increasing by 40% when the electron affinity is decreased to 0.15 eV. It must be remembered, however, that the error in the matrix element generator, Eqs. (10) and (11), is unknown for this low value of the electron detachment energy. For $O_2^- + N_2^+$, the theoretical value of $25 \times 10^{-8} \text{ cm}^3/\text{sec}$ agrees well with the experimental merged-beam value. This is puzzling when compared with the $O_2^- + O_2^+$ case, but it may be caused by a lack of excited states available for reaction in the critical R_c region. Several other O_2^- reactions of upper atmospheric interest are shown.

For the NO_2^- reactions, we have used the lower and upper limits of the electron affinity given by Berkowitz, Chupka, and Gutman.²⁴

ION-ION THERMAL ENERGY RECOMBINATION REACTION RATES:

MOLECULAR NEGATIVE ION

System	Electron Detachment Energy (eV)	R_c (a.u.)	Calculated $\alpha \times 10^8$ (cm ³ /sec)	Experimental $\alpha \times 10^8$ (cm ³ /sec)
$O_2^- + O_2^+$	0.43	36	24 ± 8	42 ± 13^a , 10 ± 1^b
$O_2^- + N_2^+$	0.43	36	25 ± 8	16 ± 5^c
$O_2^- + O^+$	0.43	35	29 ± 9	--
$O_2^- + Na^+$	0.43	36	26 ± 9	--
$O_2^- + NO^+$	0.43	36	24 ± 8	--
$NO_2^- + O_2^+$	1.83	22	13 ± 3	41 ± 13^a
	2.32	20	12 ± 3	
$NO_2^- + NO^+$	1.83	22	14 ± 3	51 ± 15^a , 17.5 ± 6^d , 21 ± 6^e
	2.32	20	12 ± 3	
$NO_3^- + O_2^+$	2.48	19	11 ± 2	13 ± 4^f
	3.20	18	10 ± 2	
$NO_3^- + NO^+$	2.48	19	11 ± 2	81 ± 23^f , 3.4 ± 1.2^b
	3.20	18	11 ± 3	

a. Reference 13.

b. Reference 16.

c. Deduced from the extrapolation of data from Reference 12.

d. Reference 15.

e. From Reference 25 with errors estimated from the extreme spread of the data.

f. Reference 20.

We find that the theoretical calculations here underestimate the merged-beam results by at least a factor of 3 for the two reactions shown. Little is known about the excited state populations produced in the beam experiments so we can only speculate that NO_2^- is possibly being formed in an excited electronic or vibrational state or that there is a gross deficiency in the theory. Another possible explanation for these large cross sections can be found in the work of Weiner, Peatman, and Berry²⁶. These authors indicate that potential curve crossings at large distances, $R_x > 100a_0$, contribute significantly and possibly dominate the cross sections. In our model, these curve crossings have a negligible effect on the cross sections. The $\text{NO}_2^- + \text{NO}^+$ reaction rate has also been measured at thermal energies by the afterglow method¹⁵ and by plasma studies.²⁵ Here the agreement between theory and experiment is satisfactory.

Only preliminary data are available on the "merged-beam" results for the NO_3^- reactions. For the cases available, there is agreement on the $\text{NO}_3^- + \text{O}_2^+$ reaction but an underestimation by theory in the $\text{NO}_3^- + \text{NO}^+$ case. The afterglow results for this latter system are below the theoretical results and in agreement with the limitations on the absorbing-sphere model. In the NO_3^- system, the electron affinity limits were again taken from the work of Berkowitz, Chupka, and Gutman.²⁴

CROSS SECTION ENERGY DEPENDENCE

The energy dependence of the cross sections may be calculated by using Eq. (7) for the evaluation of λ . In Fig. 1 are shown the predicted cross section curves for the negative ions studied here. The curves for each system are essentially independent of the mass of positive ion (within $\pm 10\%$) when the mass of the positive ion is within a factor of 2 to that of the negative ion.

As expected from the previous calculations, the system with the lowest electron affinity, O_2 , has the largest cross sections at a given energy. Likewise, the system with the largest electron affinity, NO_3 , has the smallest cross sections. If the negative ion lies in an excited level above its ground state, we would expect the observed cross sections to be larger than those predicted here.

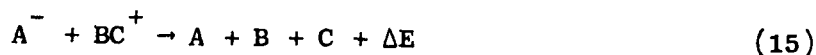
We may test the predicted cross sections with the many O^- systems that have been observed in the merged-beam work. This system was chosen because of the abundance of available data. No comparisons were made with the molecular negative ions since the reactant excited state populations are undetermined. Figure 2 draws the predicted cross section and the data from the five systems that have been measured. The energy dependence of the cross sections is very well reproduced by theory. All the cross sections lie well within a factor of two with theory with the exception of $NO^+ + O^-$ which is above the prediction throughout the energy range. As in the calculation of the reaction rates, the reason why the NO^+ ion produces such large cross sections is unexplained. However, on a relative scale, the energy dependence of the $NO^+ + O^-$ cross sections would be well reproduced.

DISCUSSION AND CONCLUSIONS

In the preceding sections, we have presented a model for estimating the upper limit cross sections for the ion-ion mutual neutralization reactions. The model is based on the Landau-Zener approximation, a semiempirical method for estimating the coupling matrix elements, and the assumption that there are a large number of states available for reaction. If there are few states available, the absorbing sphere model will definitely overestimate the reaction rate, as it did in the $H^+ + H^-$ case.

The model was set up specifically for application to molecular systems in which there are large numbers of neutral excited electronic and vibrational channels available for reaction. For systems including negative molecular ions, comparisons with merged-beam results were somewhat ambiguous because of the uncertainty in the excited state populations of the negative molecular ion beams. For the neutralization reaction rates that were measured at thermal energies by the afterglow method, the agreement with theory was satisfactory. For atomic negative ion systems in which the excited state populations of the negative ion are not a factor, agreement with the merged-beam results generally was good.

A few comments should be made concerning the significance of the dissociation reaction



since this may possibly be the source of the theoretical and experimental differences in the molecular systems. Bates and Boyd⁶ have presented the Landau-Zener formulas for this process, and we find that the absorbing-sphere model will be equally applicable to this type of reaction. The only difference between the theory for reaction (1) and that for reaction (15)

is in the energy dependence of the cross sections. At low energies, which is the region of interest for the reaction rates, both reactions (1) and (15) will have a cross section dependence approaching E^{-1} . At higher energies, however, the cross sections for reaction (1) continue to decrease, but at a rate slower than E^{-1} , until extremely high energies of $E \gtrsim 1$ keV are reached. The cross sections for reaction (15) at high energies, however, approach a constant value. The cross section energy dependence at high energies will be determined primarily by the neutral molecular states of the positive ion. We may predict that reaction (15) will be important if the neutral molecular states of the positive ion in the potential energy region of the ground state positive ion minus the electron detachment energy of the negative ion minus approximately 1 eV lead to dissociation. So far, the energy dependence of the experimental data on the molecular ions tends to indicate that the dissociation reaction is not a dominate process for those systems measured.

With regard to the vibrational change of state on reaction, the Franck-Condon factors, Eq. (14) will dictate that at large distances the transition probability for the transfer of the electron will be greatest for states with the greatest amount of vibrational overlap. Generally this means that for reactions at large distances, which determine the magnitude of the cross sections the most, the conditions are favorable for little change in the vibrational state. At smaller intermolecular separations, where the electronic matrix coupling element alone is so large that it precludes reactions, transitions to states where there is little vibrational overlap will allow a significant amount of reaction. Generally speaking, we would expect a greater change in vibrational energy to occur for reactions at small impact parameters.

Probably the most significant factor to note in this work is the large reaction rate dependence on the electron detachment energy. If the energy for the electron detachment is decreased because of populated excited states of the negative ion, the cross sections increase. If the excitation is to the upper levels, this increase becomes significant. For upper atmosphere chemistry, this fact necessitates knowing the excited state populations of the reactants for the ion-ion recombination reaction.

ACKNOWLEDGMENTS

The author wishes to thank Drs. John Moseley and James Peterson for providing reaction rates prior to publication.

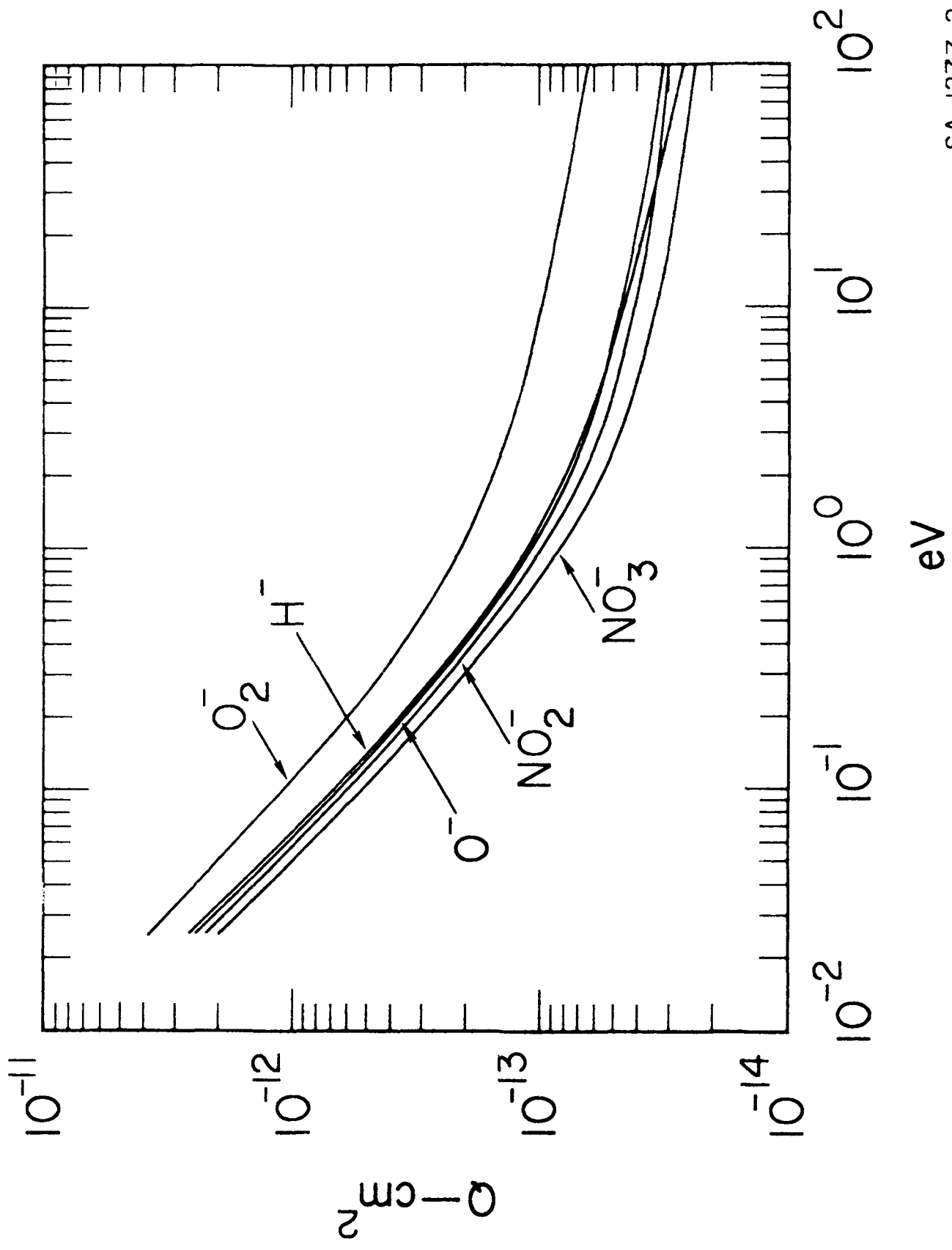
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FIGURE CAPTIONS

1. Cross section energy dependence predicted by the "absorbing-sphere" model. For each system, the cross section curve is accurate to $\pm 10\%$ for mass ratio variations of less than 2. The electron detachment energies used were: O_2 - 0.43 eV, H - 0.754 eV, O - 1.48 eV, NO_2 - 2.1 eV, and NO_3 - 3.0 eV.
2. Solid line: cross section curve predicted by the "absorbing-sphere" model for O^- systems. The electron detachment energy used for O was 1.48 eV. The data are from "merged-beam" results; references 9, 12, and 14.



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Figure 1

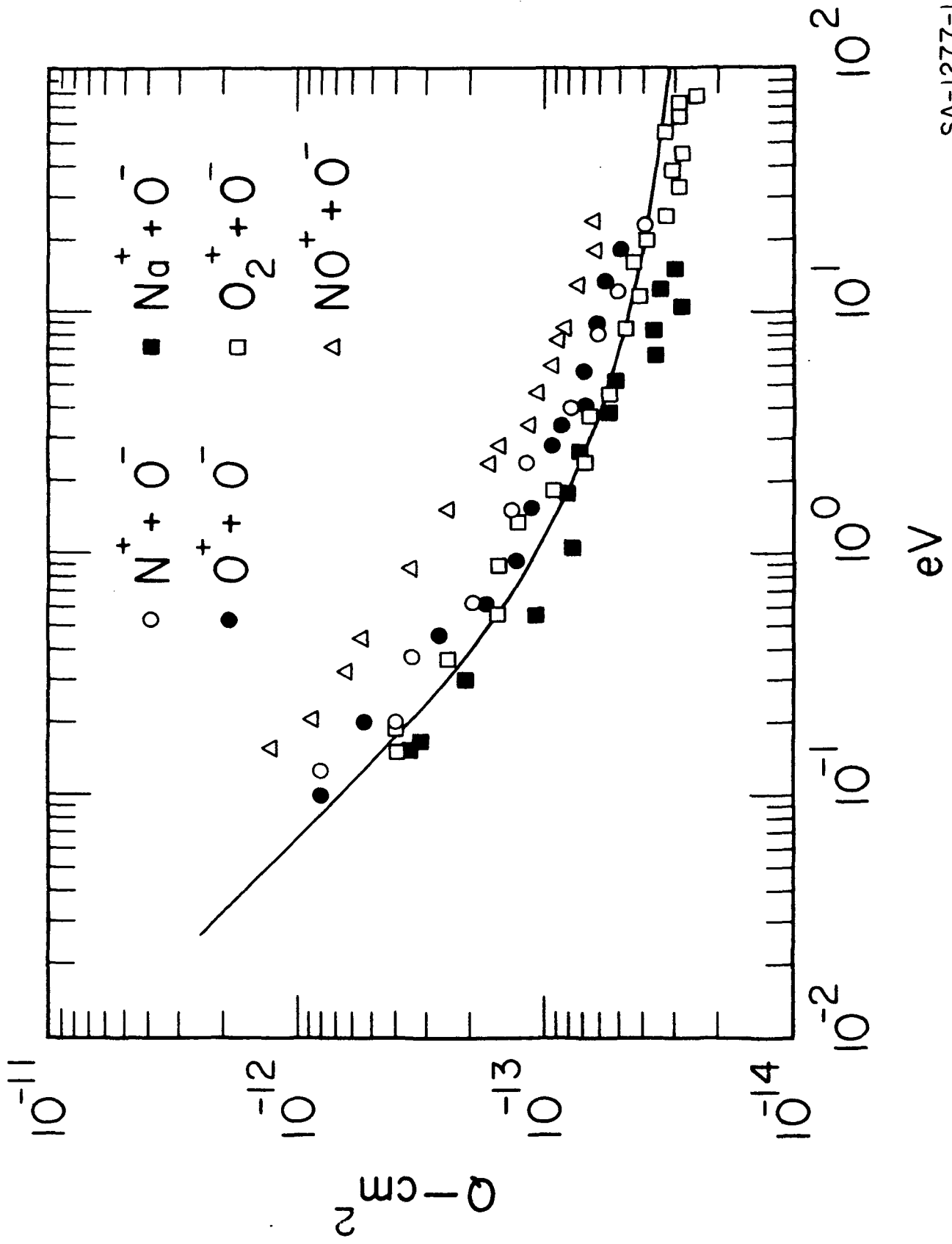


Figure 2

Appendix B

ENERGY DEPENDENCE FOR $\text{Ne}^*(2p^5 3s \ ^3P) + \text{Ar}$
IONIZATION TOTAL CROSS SECTIONS

Submitted to: Chemical Physics Letters

Energy Dependence for $\text{Ne}^*(2p^5 3s \ ^3P) + \text{Ar}$ Ionization
Total Cross Sections*

Ronald E. Olson

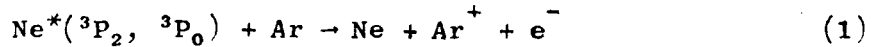
Stanford Research Institute
Menlo Park, California USA

Abstract

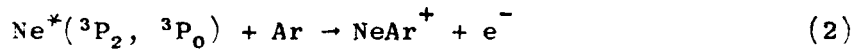
The ionization (Penning and associative) total cross sections for $\text{Ne}^*(2p^5 3s \ ^3P) + \text{Ar}$ are calculated semiclassically in the energy range of 0.001 to 1000 eV and compared with recent experimental results of Micha, Tang, and Muschlitz.

* Supported by the National Aeronautics and Space Administration and Stanford Research Institute.

The recent experimental data of Micha, Tang, and Muschlitz¹ on the low energy (0.01 to 0.1 eV) dependence of the ionization total cross sections for the sum of the Penning ionization process



and of the associative ionization process



display an unexpected energy dependence that has not been explained by theoretical calculations. These authors find cross sections that first decrease as the energy increases, then pass through a minimum, and later increase at the highest energies measured. Calculations by these authors using a Lennard-Jones, L-J, (12,6) interaction potential and a short range coupling width $\Gamma(R)$ were able to reproduce the low energy, monotonically decreasing behavior of the cross sections but did not follow the change in slope. Further experimental work by Tang, Marcus, and Muschlitz² on $\text{Ne}^* + \text{Kr}$ and $\text{Ne}^* + \text{Xe}$ show the same type of behavior. On another noble gas system -- $\text{He}^* (2^3\text{S} \text{ and } 2^1\text{S}) + \text{Ar}$ -- the thermal energy cross section^{3,4} is comparable or smaller than the high energy results at 100 to 1000 eV.⁵ It therefore appears that the shape of the energy dependence of the $\text{Ne}^* + \text{Ar}$ cross sections could be common to many of the noble gas ionization reactions.

Calculations were performed using the semiclassical formulas found in a paper by Miller⁶. Here, the ionization cross section is

$$Q = 2\pi\alpha \int_0^\infty db \cdot b \cdot P(b) \quad (3)$$

where the ionization probability is given by

$$P(b) = 1 - \exp \left\{ - 2 \int_{R_0}^{\infty} \frac{dR \Gamma(R)}{v_b(R)} \right\}. \quad (4)$$

The radial velocity is calculated from

$$v_b(R) = v_0 \left\{ 1 - V_0(R)/E - b^2/R^2 \right\}^{\frac{1}{2}} \quad (5)$$

where v_0 is the incident velocity and b is the impact parameter. In Eq. (3), ρ is the statistical weight factor that is unity for this system. The coupling to the continuum is provided by the width $\Gamma(R)$, which in this case we have assumed to be of exponential form. This form is similar to the shapes of $\Gamma(R)$ calculated by Miller, Slocumb, and Schaefer⁷; Bell⁸; and Fujii et al.⁹ for the $\text{He}^+ + \text{H}$ system and is similar to that deduced from $\text{He}^+ + \text{Na}$ experimental data by Hotop and Niehaus¹⁰. The interaction potential $V_0(R)$ is that of the metastable atom in the field of the neutral atom. Several different forms for the interaction potential were used while we restricted the coupling width to the exponential form

$$\Gamma(R) = A \exp(-BR). \quad (6)$$

We first hoped that the data could be reproduced by a potential with two minima, arising from a long range van der Waals well, a barrier at intermediate distances with a magnitude equal to the energy at which the experimental cross sections change slope, and a strong chemical well at small separations. In Figure 1, the short dashed lines show such a potential that was formed to reproduce approximately the L-J potential of Micha et al.¹ from $R \approx 7.5$ to $10 a_0$. Its functional form is given by

$$V_0(R) = 4\epsilon \left\{ \left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right\} + a \exp \left\{ -b(R-c)^2 \right\}, \quad (7)$$

and the parameters used were $\epsilon = 0.15$ a.u., $\sigma = 3.5$ a.u., $a = 2.5 \times 10^{-3}$ a.u., $b = 1.0$ a₀⁻¹, and $c = 6.75$ a₀. A second calculation was made using the L-J potential parameters of Ref. 1 that were obtained from the Slater-Kirkwood value for the long range dipole-induced dipole term and the composition rules for ϵ . The parameters are $\epsilon = 1.76 \times 10^{-4}$ a.u., $\sigma = 8.16$ a₀, and $a = b = c = 0$. This L-J potential is shown by the solid line.

In Figure 2 are displayed the experimental data and the results for the L-J potential, solid line, and for the potential with two minima, dashed line. The coupling width, Eq. (6), had the parameters $A = 0.01$ a.u. and $B = 1.0$ a₀⁻¹. For collision energies greater than the barrier height, 0.04 eV, we see the cross sections rising dramatically when compared with the L-J results. Since the experiments did not show such a rapid rise, the width was varied to try to obtain better agreement. We reduced the width for separations less than the potential barrier and set it equal to its value at $R = 6.9$ a₀ for $R < 6.9$ a₀. The results are given by the short-long dashed line, but again there is a sharp rise at $E \approx 0.04$ eV that is not borne out by the data.

Another possibility to explain the data is that $\Gamma(R)$ should be increasing faster at small R so that as the particles penetrate to smaller separations at the higher energies, the transition probability will increase. Rather than varying $\Gamma(R)$ randomly, we set $A = 1.0$ and chose B such that it best reproduced the low energy data around $v = 500$ m/sec. When the L-J potential of Ref. 1 was used, we obtained the results shown in Figure 3 by the solid line. The physical characteristics of the cross sections are well reproduced, and the value of B obtained was 1.53 a₀⁻¹, close to the exponential character of various calculated widths⁷⁻¹⁰ that vary between 1 and 2.

Since the L-J potential possesses a much too repulsive core for the higher energy work, the calculations were also performed using a Morse potential with the same minimum position and magnitude as the L-J potential. It is given by

$$V_0(R) = \epsilon \left\{ e^{-2\lambda(1-R/R_e)} - 2e^{-\lambda(1-R/R_e)} \right\} \quad (8)$$

where $a = 1.76 \times 10^{-1}$ a.u., $R_e = 9.16 a_0$, and $\rho = 6.6$. The constant ρ was chosen to reproduce approximately the repulsive potential of Abrahamson¹¹ for Na + Ar in the region of 1 to 3.5 a_0 where $V_0(R)$ decreased from approximately 1000 to 10 eV. The L-J potential in this region is 2 to 3 orders of magnitude too large. The Na + Ar potential was used since it would be closest to reproducing the electron distribution of $Ne^* + Ar$.

With the Morse potential, the low energy behavior is similar to that of the L-J potential but now at higher energies the cross sections are much larger, $\sim 10 \text{ \AA}^2$, and similar in magnitude to the $He^* + Ar$ measurements.⁵ Since the Morse potential has a more realistic repulsive core, we would expect that calculations made using it would be more accurate at high energies than the L-J results. Further experimental measurements will be needed to test the energy dependence and the magnitude of the high energy cross sections predicted by the Morse potential calculations. Also, since the width has been normalized to the $Ne^* + Ar$ low energy cross sections that are uncertain by 50%, it would be unrealistic to expect that the magnitude of the theoretical calculations at higher energies will be more accurate than a factor of 2.

Most important, however, is the fact that only one parameter in the coupling width was varied to obtain the correct normalization to the experimental data at thermal energies. Since the interaction potential between the metastable and neutral atom can be derived from other sources, estimates of the energy dependence of the ionization cross sections can be made by using the available thermal energy results.

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FIGURE CAPTIONS

1. Potentials used in the calculations: L-J (12,6) - solid line, Morse - long dashed line, and the double minima potential - short dashed line.
2. Ionization total cross sections calculated using the L-J potential and $\Gamma(R) = 0.01 \cdot \exp(-R)$ is given by the solid line. For the double minima $V(R)$ and the same $\Gamma(R)$, the results are shown by the dashed line, and for the double minima $V(R)$ and the truncated $\Gamma(R)$ the results are displayed by the short-long dash line. The experimental data of Ref. 2 are shown by the solid circles.
3. Ionization total cross sections calculated with $\Gamma(R) = \exp(-1.53R)$ and the L-J potential, solid line, and with the Morse potential, dashed line. The experimental data of Ref. 1 are shown by the solid circles.

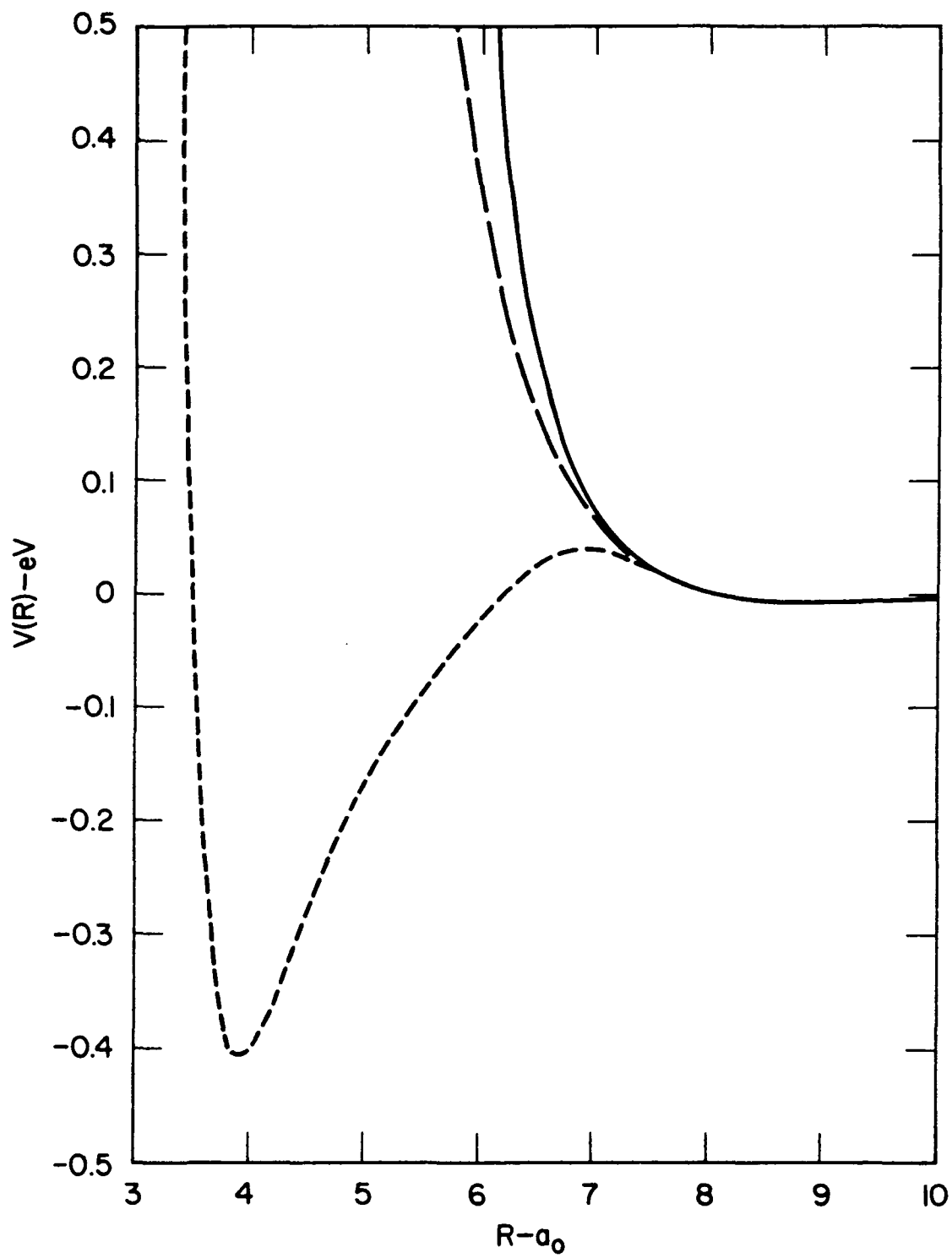
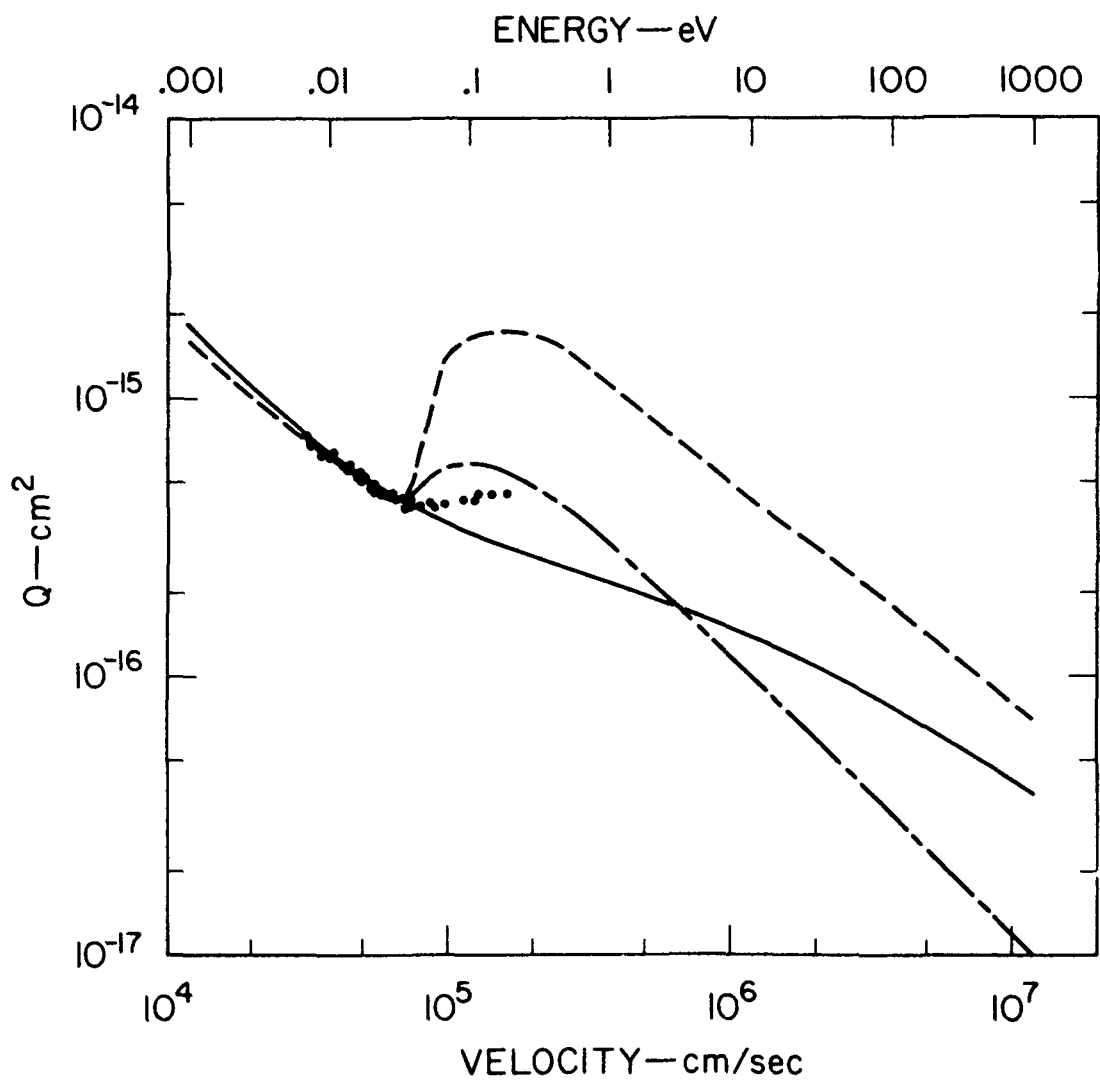
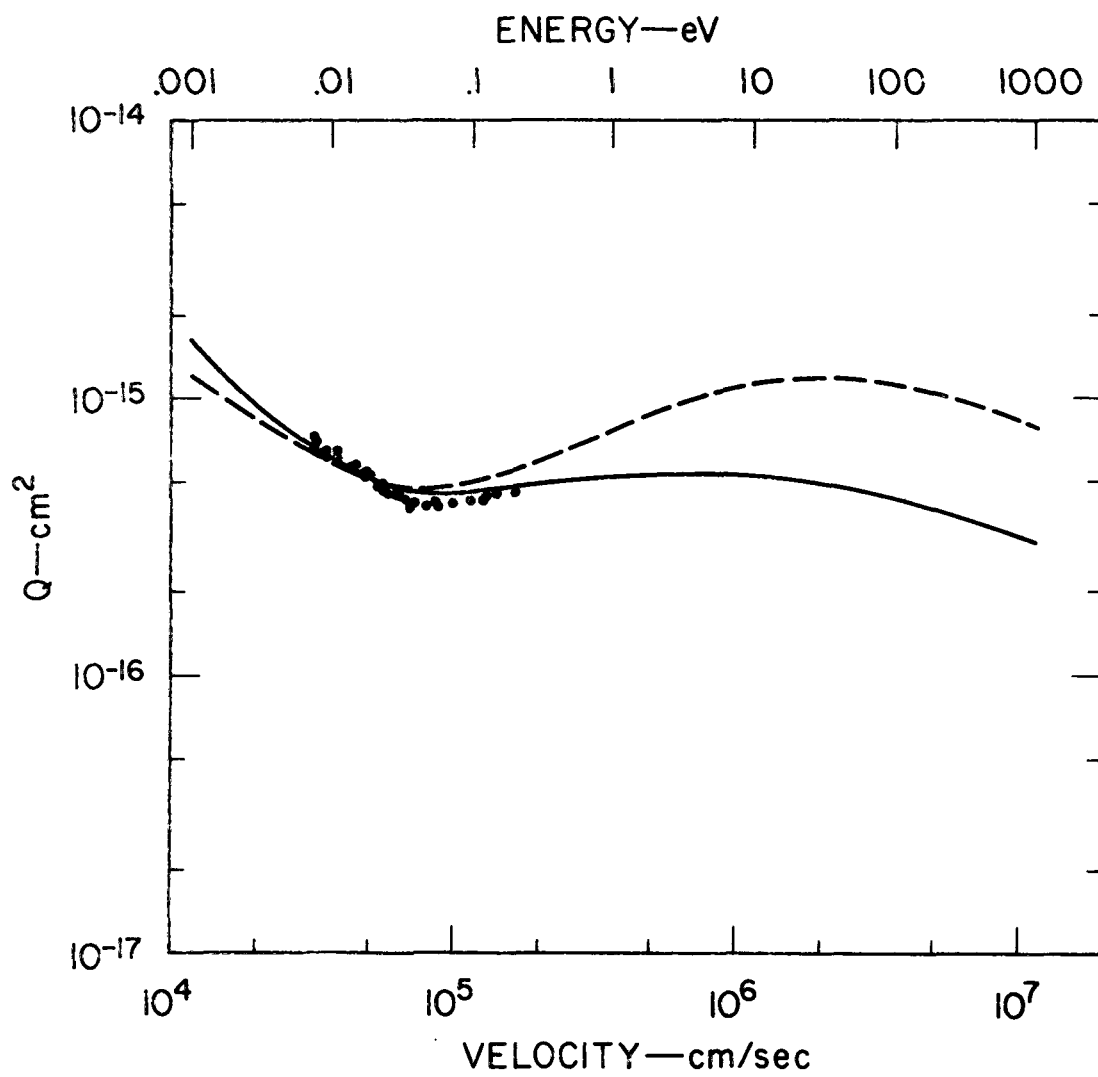


Figure 1



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Figure 2



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Figure 3